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# Daytime tropospheric loss of hexanal and *trans*-2-hexenal: OH kinetics and UV photolysis

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**Abstract.** The ultraviolet ( $\lambda=250\text{--}370\text{ nm}$ ) photolysis and the OH-initiated oxidation of hexanal and *trans*-2-hexenal, which are relevant atmospheric processes, have been investigated at room temperature and as a function of temperature ( $T=263\text{--}353\text{ K}$ ), respectively. This kinetic study as a function of temperature is reported here for the first time. Absolute absorption cross sections ( $\sigma_\lambda$ ) were obtained using a recently built system operating in the UV region. The obtained  $\sigma_\lambda$  allowed the estimation of the photolysis rates ( $J$ ) across the troposphere. Kinetic measurements of the gas-phase reaction of hydroxyl radicals (OH) with hexanal and *trans*-2-hexenal were performed by using the laser pulsed photolysis/laser-induced fluorescence technique. Rate coefficients  $k_{\text{OH}}$  for both aldehydes were determined at temperatures between 263 and 353 K at 50 Torr in helium or argon bath gases. The temperature dependence of  $k_{\text{OH}}$  for both aldehydes was found to be slightly negative. The tropospheric lifetime of hexanal and *trans*-2-hexenal due to the chemical removal by OH radicals has been estimated across the troposphere. The loss rate due to the OH chemical removal was compared with the estimated photolysis rates. Our results show that OH-reaction is the main loss process for these aldehydes in the troposphere, although photolysis is not negligible for hexanal.

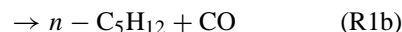
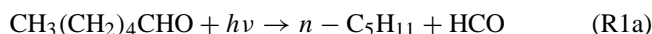
## 1 Introduction

Aldehydes are emitted into the atmosphere by different anthropogenic (they are the products of an incomplete combustion of petroleum fuels, vehicles, etc.) and natural sources (forest, pastures lawn mowing, etc.) (Grosjean et al., 2001; Kirstine et al., 1998; Owen et al., 1997; Wildt et al., 2003). These oxygenated compounds play a vital role in the for-

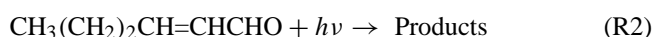
mation of photochemical smog and in the determination of levels of secondary pollutants, such as peroxyacetyl nitrate (PAN) and tropospheric ozone (Atkinson and Arey, 2003).

Photodissociation of aldehydes may also represent an important source of free radicals in the lower atmosphere, and thus may significantly influence the atmospheric oxidation capacity (Finlayson-Pitts and Pitts, 2000). The photochemistry of saturated and unsaturated  $\text{C}_6$  aldehydes, such as hexanal and *trans*-2-hexenal, has not been widely studied and a few data are available concerning the photolysis quantum yields and the absorption cross sections (Plagens, 2001; Tadic et al., 2001; Tang and Zhu, 2004). Models of urban photochemistry generally assume that photolysis of aldehydes,  $\text{RCHO}$ , yields the alkyl radical (R) and the formyl radical ( $\text{HCO}$ ), enhancing the radical flux present in the atmosphere. Tang and Zhu (2004) reported absolute quantum yields for HCO radical ( $\phi_{\text{HCO}}$ ) in the photolysis of hexanal between 305 and 320 nm in the presence of nitrogen. Tadic et al. (2001) reported total quantum yields between 275 and 380 nm in synthetic air (100–700 Torr). From the observed products in the photolysis of hexanal, these groups reported that other photodissociation channels, apart from the Norrish type I (Reaction R1a), were also possible.

For example, the molecular elimination process (Reaction R1b) and the Norrish type II (Reaction R1c):



Ultraviolet (UV) absorption cross sections ( $\sigma_\lambda$ ) for hexanal have been reported at room temperature by Tang and Zhu (2004) and by Plagens (2001). Photochemistry of *trans*-2-hexenal has been less studied:



Plagens (2001) in her PhD dissertation also reported that photolysis of *trans*-2-hexenal resulted in a fast

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photoisomerisation to *cis*-2-hexenal. The results of Plagens are in good agreement with the recently reported work of O'Connor et al. (2006).

Together with the photodissociation process, the main chemical degradation route of these aldehydes in the troposphere is thought to be the reaction with OH radicals:



Up to now, only room temperature measurements of the rate coefficients of the OH reactions ( $k_{\text{OH}}$ ) are reported for hexanal (Albaladejo et al., 2002; D'Anna et al., 2001; Papagni et al., 2000) and *trans*-2-hexenal (Albaladejo et al., 2002; Grosjean and Williams, 1992; Atkinson et al., 1995).

One of the most significant meteorological impacts in modelling ozone concentrations is the temperature reduction with the altitude in the troposphere, which alters chemical reaction rates. Thus, the use of rate coefficient expressions rather than simple rate coefficients permits simulations over a wide range of temperatures for urban, suburban, rural and remote regions and seasons of the troposphere. Since there have been only room temperature measurements of the rate coefficients for Reactions (R3) and (R4), a kinetic study on these reactions as a function of temperature is presented here for the first time, in order to give a T-expression of  $k_{\text{OH}}$  which could be used in the evaluation of the impact of these aldehydes in PAN and ozone formation.

Additionally, measurements of  $\sigma_\lambda$  for both aldehydes are also reported in this paper in order to compare the contribution of the photolysis process and the reaction with OH radicals to the tropospheric degradation of these C<sub>6</sub> aldehydes.

## 2 Experimental details

### 2.1 UV absorption cross section determination

The experimental setup employed in the determination of absolute absorption cross sections was the same as in our previous work (Jiménez et al., 2005a), therefore, only a brief description is given here. The system consisted of a Pyrex cell sealed with quartz windows, a light source and a detection system. A wide emission (200–800 nm) deuterium lamp was employed as a light source to irradiate the sample and the transmitted radiation was focused onto a 0.5-m spectrograph and detected by a CCD. The absorption cell was filled with different pressures of pure vapours of hexanal (0.9–7.0 Torr) or *trans*-2-hexenal (0.6–3.5 Torr), measured by using a pressure transducer.

The UV absorption spectra of hexanal and *trans*-2-hexenal were recorded at room temperature in the wavelength range from 210 to 370 nm with a spectral resolution of 0.2 nm. The absorption spectrum of hexanal exhibits a weak absorption between 240 and 350 nm as a result of the symmetry-forbidden  $n \rightarrow \pi^*$  transition in the carbonyl group. This band

appears shifted to longer wavelengths for *trans*-2-hexenal due to conjugation between the double bond and the C=O group. In addition to this weak band, *trans*-2-hexenal absorption spectrum shows a strong band corresponding to the  $\pi \rightarrow \pi^*$  transition in the double bond. This transition has not been characterized in this work because of its little interest from the tropospheric point of view.

Examples of the  $n \rightarrow \pi^*$  band for hexanal recorded at three different pressures are shown in Fig. 1a. A series of experiments was carried out (usually 5–6 independent determinations) at each pressure,  $p$ , under static conditions. The absorption cross section in base  $e$  at each wavelength ( $\sigma_\lambda$ ) was obtained by applying the Beer-Lambert law in terms of pressure:

$$A_\lambda = \ln(I_0/I) = \sigma_\lambda \ell p \quad (1)$$

$A_\lambda$  is the absorbance,  $I_0$  and  $I$  are the transmitted light intensity measured in the absence and in the presence of aldehyde, respectively, and  $\ell(\pm 2\sigma)$  is the optical path length ( $(107.0 \pm 0.2)$  cm). Figure 1b shows several examples of the plots of Eq. (1). From the slope of these plots,  $\sigma_\lambda$  was determined. As it can be seen in this figure, no deviation of the Beer-Lambert law was observed over the studied range of pressures.

### 2.2 OH kinetic measurements

Absolute rate coefficients,  $k_{\text{OH}}$ , for hexanal and *trans*-2-hexenal were obtained by the pulsed laser photolysis/ laser-induced fluorescence (PLP-LIF) technique as a function of temperature (263–353 K). The PLP-LIF setup, technique, and methodology have been already described in previous studies (Jiménez et al., 2005a, b). However, a brief description is given below.

Gas-phase reaction of OH radicals with hexanal or *trans*-2-hexenal takes place at the centre of a 200-cm<sup>3</sup> Pyrex reactor. OH(X<sup>2</sup>Π) radicals were generated by the pulsed photolysis of H<sub>2</sub>O<sub>2</sub>(g) at 248 nm by using a KrF excimer laser. Gas-phase H<sub>2</sub>O<sub>2</sub> was introduced in the reaction cell by bubbling the carrier gas (He or Ar) through a pre-concentrated liquid sample of hydrogen peroxide (Jiménez et al., 2005a). H<sub>2</sub>O<sub>2</sub> concentrations in the reaction cell, measured optically as described in our previous paper (Jiménez et al., 2005a) were  $(1.1\text{--}2.4) \times 10^{14}$  molecule cm<sup>-3</sup>. Therefore, OH concentration can be estimated from the known H<sub>2</sub>O<sub>2</sub> concentration, taking into account the absorption cross section of H<sub>2</sub>O<sub>2</sub> at 248 nm, the quantum yield for OH production (Sander et al., 2002), and the photolysis laser fluence  $((1.3\text{--}20.0) \text{ mJ pulse}^{-1} \text{ cm}^{-2})$ . OH radical concentration was varied from  $3.0 \times 10^{11}$  molecule cm<sup>-3</sup> to  $1.1 \times 10^{12}$  molecule cm<sup>-3</sup>. Typically, OH concentration was lower than  $7.0 \times 10^{11}$  molecule cm<sup>-3</sup> to ensure that no kinetic complications arise from the possible OH-secondary chemistry. However, some experiments were performed at concentrations up to  $10^{12}$  cm<sup>-3</sup> to check for this possibility. Under

these experimental conditions no significant influence of secondary chemistry was observed (see Results and discussion section). At different reaction times, OH radicals were excited at 282 nm ( $\text{OH}(\text{A}^2\Sigma^+, v'=1) \leftarrow \text{OH}(\text{X}^2\Pi, v''=0)$ ) by using the frequency-doubled output of a dye laser pumped by a Nd-YAG laser (operating at a repetition rate of 10 Hz). LIF signal from  $\text{OH}(\text{A}^2\Sigma^+)$  was detected at  $\lambda \geq 282$  nm by a photomultiplier tube placed orthogonal to both light sources. LIF emissions were selected by a bandpass filter (90% transmittance at 350 nm and 150 nm of FWHM) and transferred to a personal computer for analysis. Fluorescence from aldehydes that could interfere with OH detection was not observed.

### 2.2.1 Aldehyde concentrations

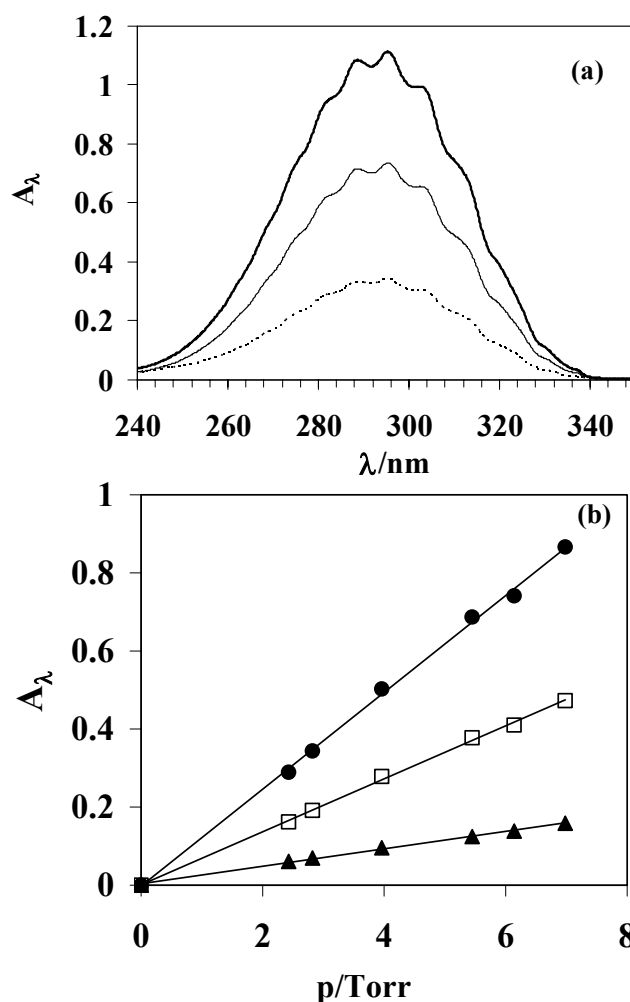
Hexanal and *trans*-2-hexenal concentrations were measured by UV absorption spectroscopy at 185 nm. Firstly, the absorption cross section of both aldehydes was measured at that wavelength using a similar methodology than that described in the previous Sect. 2.1. The experimental system employed in these measurements has been recently setup. This setup consists in a Pyrex absorption cell (in this case, we used the 107-cm long cell described in Sect. 2.1), a low power light source (a Hg/Ar pen ray lamp from Oriel) and a detection system (a Hamamatsu phototube, model R5764). The absorption cell was irradiated by the Hg/Ar pen ray lamp. The transmitted 185-nm radiation was selected by an interference filter (Andover, centred at 182.8 nm with a transmittance of 19%, FWHM of 26 nm), and collected by the phototube. The transmitted intensity in the absence ( $I_0$ ) or in the presence of aldehyde ( $I$ ) was, then, monitored by a picoamperemeter (Keithley Instruments, model 6485).

Aldehydes were diluted in 760 Torr of the bath gas and stored in a 10-L blackened bulb. Usually, the dilution factor was set to 0.2–0.6%. A known pressure of this diluted aldehyde ( $p_T=47\text{--}70$  Torr) was introduced into the absorption cell. Absorption cross sections (in base  $e$ ) at 185 nm ( $\sigma_{185\text{ nm}}$ ) were obtained, under static conditions, by applying Beer-Lambert law (Eq. 1). The average of 4–5 measurements of the absorption cross sections ( $\pm 2\sigma$ ) were found to be  $(9.37 \pm 0.32) \times 10^{-18} \text{ cm}^2$  for hexanal and  $(1.07 \pm 0.07) \times 10^{-17} \text{ cm}^2$  for *trans*-2-hexenal.

Secondly, knowing  $\sigma_{185\text{ nm}}$  for each aldehyde, their concentrations can be determined by using the following equation:

$$[\text{RCHO}]_{\text{UV cell}} = \frac{\ln(I_0/I)}{\ell \times \sigma_{185\text{ nm}}} \quad (2)$$

During the kinetic measurements, a flow of diluted aldehyde ( $f_{\text{aldehyde}}$ ), a flow of the carrier gas through  $\text{H}_2\text{O}_2(\text{aq.})$  ( $f_{\text{peroxide}}$ ), and the main flow of bath gas ( $f_{\text{bath}}$ ) were introduced into the Pyrex reaction cell. The total flow rate was varied from 260 to 520 sccm (standard cubic centimetre per minute), corresponding to a linear velocity between 5 and  $15 \text{ cm s}^{-1}$ . Under flowing conditions, aldehyde concentrations were measured before and after entering the reaction

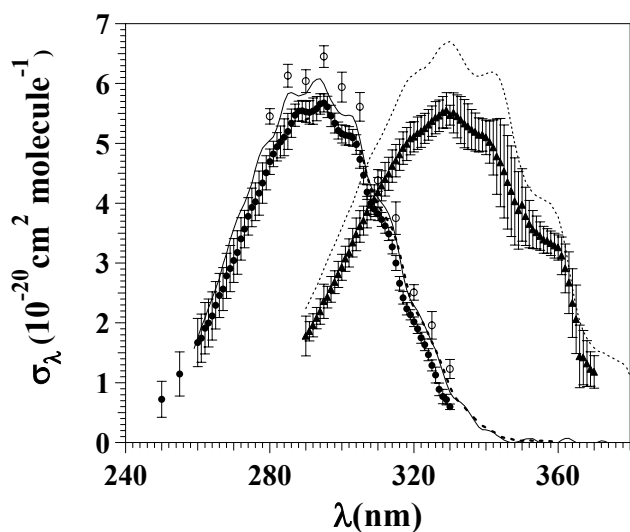


**Fig. 1.** (a) Absorption spectra for hexanal recorded at 1.07 (dashed line), 3.09 (thin line), and 5.01 Torr (thick line). (b) Beer-Lambert law plots at 310 nm (●); 320 nm (□), and 330 nm (▲).

cell. A difference of 7% for hexanal and 14% for *trans*-2-hexenal between both measurements was observed. These differences were found to be independent of the linear velocity and the laser fluence in the range studied. Based on the measured absorption cross section, the expected aldehyde loss in the reaction cell due to photolysis at 248 nm is much less than 1%.

When aldehyde concentrations were measured before entering the reactor, the aldehyde is introduced into the absorption cell from the bulb, the rest of flows are introduced directly into the reaction cell. Thus, a correction has to be made in the measured  $[\text{RCHO}]_{\text{UV cell}}$  in order to account for the further dilution in the reaction cell and the differences in temperature and pressure between the UV cell and the reactor. The expression for this correction was:

$$[\text{RCHO}]_{\text{reactor}} = [\text{RCHO}]_{\text{UV cell}} \frac{f_{\text{aldehyde}}}{f_{\text{Total}}} \frac{p_{\text{reactor}}}{p_{\text{UV cell}}} \frac{298 \text{ K}}{T_{\text{reactor}}} \quad (3)$$



**Fig. 2.** Absorption spectra for hexanal (●) and *trans*-2-hexenal (▲) reported in this work. Comparison of the  $\sigma_\lambda$  determined in this work for hexanal and *trans*-2-hexenal with those found in the bibliography (solid line from Plagens, 2001, dashed lines from O'Connor et al., 2006, and open circles from Tang and Zhu, 2004).

where  $f_{\text{Total}} = f_{\text{aldehyde}} + f_{\text{peroxide}} + f_{\text{bath}}$ . Only the correction in temperature was needed when the RCHO concentrations were measured at the exit of the reactor. Aldehyde concentrations obtained were  $(0.2\text{--}2.7) \times 10^{14}$  molecule  $\text{cm}^{-3}$  for hexanal and  $(0.1\text{--}5.2) \times 10^{14}$  molecule  $\text{cm}^{-3}$  for *trans*-2-hexenal. Also, aldehyde concentrations were determined from gas flow rate measurements using calibrated mass flow meters and the total pressure inside the reaction cell. The difference found between both methods for hexanal was about 10% and between 8 and 24% for *trans*-2-hexenal. Optically measurements of aldehyde concentration were used in this work.

### 2.2.2 Reactants

He (Carbueros Metálicos, 99.999%) and Ar (Praxair, 99.999%) were used as bath gas without additional purification. Samples of hexanal (Aldrich, 98%) and *trans*-2-hexenal (Aldrich, 98%) were purified by freeze/pump/thaw cycles. Aqueous solution of  $\text{H}_2\text{O}_2$  (Sharlau, 50% w/v) was treated as described earlier (Jiménez et al., 2005a).

## 3 Results and discussion

### 3.1 UV absorption cross sections ( $\sigma_\lambda$ )

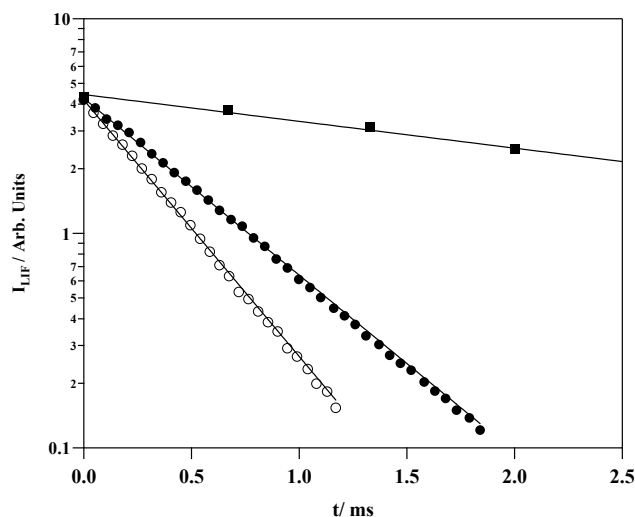
The weighted average of  $\sigma_\lambda$  for hexanal (from 250 to 330 nm) and *trans*-2-hexenal (from 290 to 370 nm) determined in this work are listed for every nm in Table 1S of the supplementary information (<http://www.atmos-chem-phys.net/7/1565/2007/acp-7-1565-2007-supplement.pdf>). The weighting

factor ( $w_i$ ) was defined as the reciprocal of the variance of each absorption cross section ( $1/\sigma_i^2$ ). The uncertainty in the absorption cross sections is estimated to be  $\sim 4\%$  at the absorption maximum and represents twice the standard deviation from the weighted average. These data are also shown in Fig. 2, where the measured  $\sigma_\lambda$  as a function of wavelength are plotted for both aldehydes. As it can be seen in this figure,  $\sigma_\lambda$  is on the order of  $10^{-20}$   $\text{cm}^2$  in both cases.

The absorption maximum around 295 nm for hexanal and 329 nm for *trans*-2-hexenal corresponds to the  $n \rightarrow \pi^*$  transition ( $\text{C}=\text{O}$  chromophore). Conjugation makes the maximum move to longer wavelengths ( $\lambda \geq 290$  nm) in *trans*-2-hexenal, and the whole band lies in the actinic region. This fact indicates that photolysis can be an important removal pathway for this aldehyde in the troposphere.

As far as we know, there are two previous studies on the absorption cross sections of hexanal (Plagens, 2001; Tang and Zhu, 2004). Plagens (2001) determined  $\sigma_\lambda$  between 259 and 375 nm and the data are listed in the on-line database (Keller-Rudek and Moorgart, 2006). More recently, Tang and Zhu (2004) measured  $\sigma_\lambda$  in the 280–330 nm spectral range every 5 nm (11 discrete wavelengths). The spectral range recorded in both studies is similar to that of this work. Plagens (2001) and Tang and Zhu (2004) found that the maximum absorption cross section at 295 nm was  $(6.03 \pm 0.12) \times 10^{-20}$   $\text{cm}^2$  and  $(6.45 \pm 0.18) \times 10^{-20}$   $\text{cm}^2$ , respectively. More recently, O'Connor et al. (2006) pointed out the good agreement between our previously reported value  $((5.68 \pm 0.15) \times 10^{-20}$   $\text{cm}^2$ ) (Jiménez et al., 2006) and their maximum absorption cross section of  $5.67 \times 10^{-20}$   $\text{cm}^2$  at 295 nm. The maximum  $\sigma_\lambda$  found by Plagens (2001) and Tang and Zhu (2004) are around 10% higher than that found by O'Connor et al. (2006) and that reported in this work. This small difference can be attributed to a systematic error in the measurement of the pressure inside the absorption cell. An underestimation or overestimation of 10% especially at low pressures (0.9–7 Torr in this work and 0.5–8 Torr in Tang and Zhu's work) can lead to the observed difference. Another possible reason for the difference observed was pointed out by Tang and Zhu (2004). These authors attributed to a possible drop in the dye-laser fluence used in their experiments the slightly higher absorption cross sections measured respect to those of Plagens (2001). A comparison of all these measurements with those from this work is presented in Fig. 2.

Simultaneously to our measurement of the absorption cross sections for *trans*-2-hexenal, O'Connor et al. (2006) has recently performed a similar study between 290 and 400 nm. These authors compared our previously reported value of  $\sigma_\lambda$  at 329 nm,  $(5.55 \pm 0.30) \times 10^{-20}$   $\text{cm}^2$  (Jiménez et al., 2006), with their measured value of  $6.68 \times 10^{-20}$   $\text{cm}^2$ . As Fig. 2. shows their absorption cross sections are systematically higher than ours. Even though, no uncertainties in the measured absorption cross sections were reported by O'Connor et al. (2006), they concluded that there is a good agreement with our value. Taking into account the



**Fig. 3.** Temporal profiles of the OH LIF signal recorded in the absence (■) and in the presence of  $5.5 \times 10^{13} \text{ cm}^{-3}$  of hexanal (●) and *trans*-2-hexenal (○) at 298 K.

experimental difficulties in handling the unsaturated aldehyde, we can consider the difference observed within the experimental errors.

### 3.2 OH kinetic measurements

In this kinetic study, the disappearance of OH radical in the reactor is mainly due to its reaction with hexanal (Reaction R3) or *trans*-2-hexenal (Reaction R4). However, its reaction with  $\text{H}_2\text{O}_2$  (Reaction R5) and the diffusion loss (Reaction R6) have to be considered as well:



Under pseudo-first order conditions, the temporal profiles of OH radical are described by Eq. (4):

$$[\text{OH}]_t = [\text{OH}]_0 \exp(-k' t) \quad (4)$$

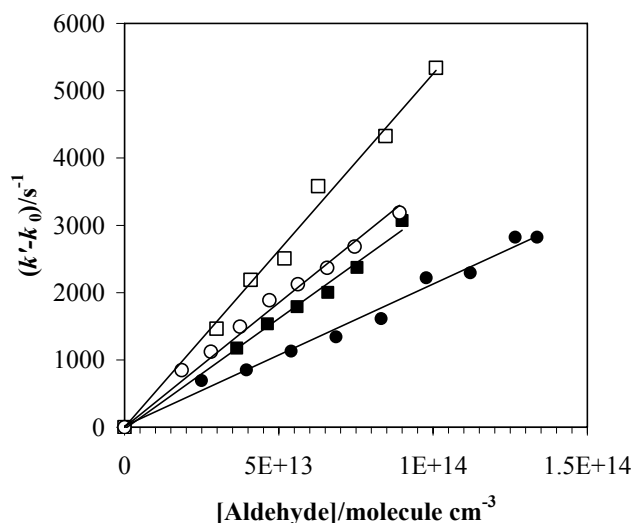
where  $k'$  is the pseudo-first order rate coefficient defined as:

$$k' = k_{\text{OH}}[\text{RCHO}] + k_0 \quad (5)$$

and  $k_0$  is the rate coefficient determined in the absence of aldehyde:

$$k_0 = k_{\text{prec}}[\text{H}_2\text{O}_2] + k_{\text{diff}} \quad (6)$$

$k'$  ( $1138\text{--}8880 \text{ s}^{-1}$ ) and  $k_0$  ( $84\text{--}1260 \text{ s}^{-1}$ ) values are extracted from the analysis of the exponential curves of the OH LIF signal ( $I_{\text{LIF}} \propto [\text{OH}]_t$ ) versus reaction time. In order to ensure that pseudo-first order conditions are reached and no secondary chemistry at long reaction times is acting, semilog plots of the exponential decays were checked. Two examples



**Fig. 4.** Pseudo-first order plots of  $k' - k_0$  versus aldehyde concentration for hexanal (filled symbols) and *trans*-2-hexenal (open symbols) at 263 K (squares) and 353 K (circles).

of the linearised Eq. (4) (in terms of the LIF signal) are presented in Fig. 3 recorded in the absence and in the presence of aldehyde at room temperature. The good linearity (over more than three OH-lifetimes) of these plots indicates that there is no significant interference of OH-secondary chemistry.

$k'$  values were always corrected for the reaction of OH with  $\text{H}_2\text{O}_2$  (Reaction R5) and the diffusion loss (Reaction R6). The bimolecular rate coefficient  $k_{\text{OH}}$  was determined by plotting  $k' - k_0$  versus the aldehyde concentration. An example of these plots at 263 and 353 K is shown in Fig. 4 for both aldehydes. As can be seen in this figure, the slopes (and, therefore,  $k_{\text{OH}}$ ) are higher for *trans*-2-hexenal than for hexanal at all temperatures. OH rate coefficients for *trans*-2-hexenal are almost twice than that found for hexanal.

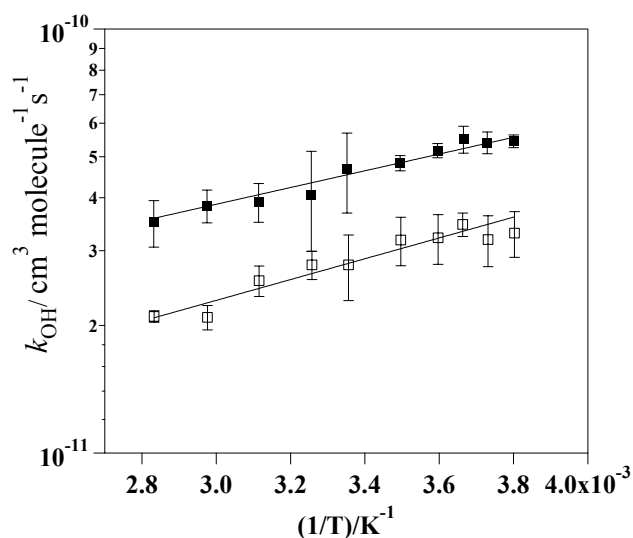
#### 3.2.1 Room temperature measurements

In Table 1, the rate coefficients  $k_{\text{OH}}$  for both aldehydes at room temperature are listed and compared with those of previous studies on the same reactions. These values are the weighted averages of several measurements performed at 50 Torr (weighting factor,  $w_i = 1/\sigma_i^2$ ). As it can be seen, our reported  $k_{\text{OH}}$  (298 K) for hexanal is in excellent agreement, within the error limits given, with previous absolute measurements carried out in our laboratory (Albaladejo et al., 2002) and other relative measurements performed at atmospheric pressure (Papagni et al., 2000; D'Anna et al., 2001). Regarding  $k_{\text{OH}}$  (298 K) for *trans*-2-hexenal, there are several studies (Atkinson et al., 1995; Grosjean and Williams, 1992; Albaladejo et al., 2002) which are in reasonable agreement with the one reported here. The difference between our previously reported  $k_{\text{OH}}$  (298 K) for *trans*-2-hexenal (Albaladejo et al., 2002) and the one measured in this work is probably

**Table 1.** Comparison of the OH rate coefficient at 298 K obtained in this work with previous studies.

Aldehyde	$p_T$ (Torr)	$k_{OH} \times 10^{11}$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	Technique	Reference
hexanal	50	$2.78 \pm 0.50$	PLP-LIF	This work
	100–400	$2.60 \pm 0.21$	PLP-LIF	Albaladejo et al. (2002)
	760	$2.86 \pm 0.13$	RR-FTIR	D'Anna et al. (2001)
	740	$3.17 \pm 0.15$	RR-GC	Papagni et al. (2000)
<i>trans</i> -2-hexenal	50	$4.68 \pm 0.50$	PLP-LIF	This work
	100–400	$2.95 \pm 0.45$	PLP-LIF	Albaladejo et al. (2002)
	760	3.10	Estimated	Grosjean and Williams (1992)
	740	$4.41 \pm 0.94$	RR-GC	Atkinson et al. (1995)

<sup>a</sup> PLP-LIF, pulsed laser photolysis-laser induced fluorescence; RR, relative rate

**Fig. 5.** Arrhenius plots for the reactions of OH radicals with hexanal (□) and *trans*-2-hexenal (■).

due to the different method used to measure the gas-phase concentration of *trans*-2-hexenal. In that case, the aldehyde concentration was calculated using flow measurements.

As can be seen from data in Table 1, total pressure (50–760 Torr) and bath gas (He, Ar or air) have no effect on the measured rate coefficients. The absence of pressure dependence of  $k_{OH}$  is relevant for building structure-activity relationships. At room temperature, our results are consistent with the values obtained from the structure-activity relationship (SAR) (Kwok and Atkinson, 1995). For the Reaction (R3), SAR method predicts that 72% of the H-atom abstraction is expected to occur from the CHO group. The OH-attack to the hydrogen atom in  $\gamma$ -position in the carbon chain accounts for approximately 16% and the rest of channels accounts each one for less than 5%. The rate coefficient for this OH-reaction is calculated to be  $2.88 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , in excellent agree-

ment with our experimental value ( $(2.78 \pm 0.50) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). The product branching ratios derived from the different attacks predicted by the SAR method have not been confirmed experimentally. As far as we know, the results on the product study of the reaction of hexanal with OH (Reaction R3) in the presence of  $\text{NO}_x$  at 1 bar of synthetic air reported by Plagens (2001) are the only available data. These results showed that H-atom abstraction from the aldehydic group (R3a) is important:



Further reaction of the hexanoyl radical ( $\text{CH}_3(\text{CH}_2)_4\text{CO} \cdot$ ) with  $\text{O}_2$  and  $\text{NO}_x$  forms hexanoylperoxynitrates (31–43% of the abstraction channel), pentanal and  $\delta$ -hydroxypentanal (both 23–28% of the abstraction channel) and 1-pentynitrates (20–23% of the abstraction channel). All these products were detected by the Gas-Chromatography with Mass Spectrometry (GC-MS) technique. Concerning other reaction products of R3 no information has been reported, yet.

For the reaction of OH radicals with *trans*-2-hexenal (R4), SAR method predicts that the rate coefficient for the OH-addition to the double bond is  $2.17 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $1.93 \times 10^{-11}$  for the H-abstraction channel. That means that the addition channel is expected to be more than 50% of the total rate coefficient ( $4.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). This calculated rate coefficient (although, 14% lower) is in excellent agreement with our experimental results ( $(4.68 \pm 0.50) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). H-atom abstraction from aldehydic group is also expected to be the major abstraction pathway (87%). No product studies have been reported for the Reaction (R4), which could confirm the predicted product branching ratios.

### 3.2.2 Temperature dependence of $k_{OH}$

The obtained rate coefficients  $k_{OH}$  as a function of temperature ( $T=263$ – $353 \text{ K}$ ) are presented in Table 2 for hexanal and *trans*-2-hexenal.  $k_{OH}(T)$  are the weighted average of several

**Table 2.** Averaged rate coefficients ( $k_{\text{OH}}$ ) as a function of temperature for the gas-phase reaction of OH radicals with hexanal and *trans*-2-hexenal.

T (K)	$(k_{\text{OH}} \pm 2\sigma) \times 10^{11} \text{ (cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\text{)}$	
	hexanal	<i>trans</i> -2-hexenal
263	3.30±0.40	5.44±0.20
268	3.19±0.44	5.40±0.32
273	3.46±0.22	5.50±0.40
278	3.22±0.44	5.17±0.20
286	3.18±0.40	4.83±0.20
298	2.78±0.50	4.68±1.00
307	2.78±0.22	4.07±1.10
321	2.55±0.22	3.91±0.41
336	2.09±0.14	3.83±0.34
353	2.10±0.07	3.50±0.44

measurements at each temperature and the error bars account for twice the standard deviation that include any systematic error. In Fig. 5, Arrhenius plots are presented for the rate coefficients listed in Table 2. Solid lines represent the fit to the experimental data. The resulting Arrhenius expressions ( $\pm 2\sigma$ ) are:

Hexanal:  $k_{\text{OH}}(\text{T}) = (4.2 \pm 0.8) \times 10^{-12} \exp((565 \pm 65)/\text{T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

*trans*-2-hexenal:  $k_{\text{OH}}(\text{T}) = (9.8 \pm 2.4) \times 10^{-12} \exp((455 \pm 80)/\text{T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

This study represents the first report of the temperature dependence of  $k_{\text{OH}}$  for hexanal and *trans*-2-hexenal. However, J. B. Burkholder's group (private communication) has performed a simultaneous study on the temperature dependence of the OH+*trans*-2-hexenal reaction (T=244–374 K), observing a negative activation energy, which is in agreement with our results.

Negative activation energies for both reactions were found to be in concordance with the temperature dependence observed for other aldehydes (Atkinson and Arey, 2003). As can be seen in Table 3, the  $E_a/R$  values obtained for the reactions of *trans*-2-hexenal and hexanal with OH are similar, which is also in accordance with previous results for other saturated and unsaturated aldehydes. Despite the negative temperature dependence observed for  $k_{\text{OH}}$  in the reaction with hexanal, the main reaction pathway for the reaction of saturated aldehydes with OH radicals seems to be H-atom abstraction from the CHO group (Albaladejo et al., 2002; Atkinson and Arey, 2003). This behaviour could be explained by the formation of an OH-addition complex, as pointed out by Smith and Ravishankara (2002), even though a pressure dependence of the rate coefficient was not observed (see Table 1). On the other hand, the negative temperature dependence observed in  $k_{\text{OH}}$  for *trans*-2-hexenal together with the value obtained at room temperature (40% higher than the rate coefficient for hexanal) could indicate

**Table 3.** Comparison of the activation energies between some saturated and unsaturated aldehydes.

Saturated aldehyde	$E_a/R$ (K)	Unsaturated aldehyde	$E_a/R$ (K)
propanal	−405 <sup>a</sup>	acrolein	−333 <sup>c</sup>
butanal	−410 <sup>a</sup>	crotonaldehyde	−533 <sup>c</sup>
pentanal	−310 <sup>a</sup>	<i>trans</i> -2-pentenal	−510 <sup>d</sup>
hexanal	−565 <sup>b</sup>	<i>trans</i> -2-hexenal	−455 <sup>b</sup>

<sup>a</sup> Atkinson and Arey (2003); <sup>b</sup> This work; <sup>c</sup> Magneron et al. (2002); <sup>d</sup> J. B. Burkholder, private communication.

that the addition channel for the unsaturated aldehydes is not negligible, similarly to other aldehydes (Magneron et al., 2002). Further investigations on the reaction products of Reaction (R4) are required to better understand the reaction mechanism.

## 4 Atmospheric implications

The contribution of the photolysis process in the actinic region ( $\lambda \geq 290 \text{ nm}$ ) and the chemical removal by the reaction with OH radicals to the total loss rate for these aldehydes has been calculated in order to estimate the atmospheric fate of hexanal and *trans*-2-hexenal. For ease of presentation, the estimation of the rate loss for each process and the total rate loss for both aldehydes has been described separately.

### 4.1 Photolysis rate estimation

The photolysis rate coefficient,  $J_i(\theta, z)$ , for a given compound in the actinic region at a certain zenith angle ( $\theta$ ) and altitude ( $z$ ) can be estimated by solving the integral (Finlayson-Pitts and Pitts, 2000):

$$J_i(\theta, z) = \int_{\lambda_1 \geq 290 \text{ nm}}^{\lambda_2} \sigma_\lambda \phi_\lambda F(\lambda, \theta, z) d\lambda \quad (7)$$

Here  $F(\lambda, \theta, z)$  is the solar actinic flux (in photons  $\text{cm}^{-2} \text{ s}^{-1} \text{ nm}^{-1}$ ) which are usually reported for a given wavelength range ( $\Delta\lambda$ ). For that reason, the photolysis rate can be expressed as follows:

$$J_i(\theta, z) \cong \sum_{\lambda_1 \geq 290 \text{ nm}}^{\lambda_2} \sigma_\lambda \phi_\lambda F(\lambda, \theta, z) \Delta\lambda \quad (8)$$

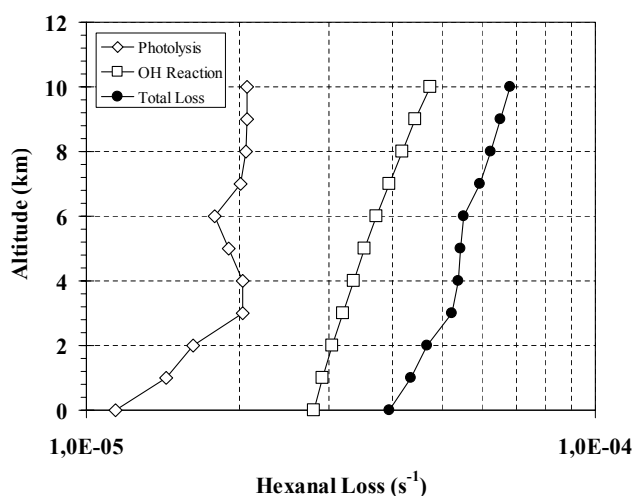
Even though, the unsaturated aldehydes possess absorption spectra in the actinic region, the reported photolysis quantum yields  $\phi_\lambda$  are nearly zero (Moortgat, 2001; O'Connor et al., 2006). Plagens (2001) and O'Connor et al. (2006) observed a fast photoisomerisation of *trans*-2-hexenal from the measurements carried out in EUPHORE under natural light conditions. In both studies, no photolysis products were detected. Thus, unless the atmospheric fate of the *cis* isomer



**Table 4.** Estimated aldehyde lifetimes, together with photolysis and OH-chemical removal rates for hexanal, as a function of altitude ( $z$ ) in the troposphere.

$z$ (km)	$T$ (K)	$J_1$ ( $10^{-5} \text{ s}^{-1}$ ) <sup>a</sup>	$k_{\text{OH}}(T)[\text{OH}]_{\text{avg}}$ ( $10^{-5} \text{ s}^{-1}$ )	$\tau_{\text{hexanal}}$ (h)	$\tau_{\text{trans-2-hexenal}}$ (h)
0	298.15	1.14	2.79	7.06	6.13
1	291.65	1.44	2.91	6.38	5.93
2	285.15	1.62	3.05	5.95	5.72
3	278.65	2.03	3.19	5.32	5.51
4	272.15	2.02	3.35	5.17	5.30
5	265.65	1.90	3.52	5.12	5.09
6	259.15	1.79	3.72	5.05	4.88
7	252.65	2.00	3.93	4.68	4.66
8	246.15	2.06	4.17	4.46	4.45
9	239.65	2.07	4.44	4.27	4.23
10	233.15	2.07	4.74	4.08	4.01

<sup>a</sup> Photolysis quantum yield taken as 0.28 at all wavelengths and altitudes (see text).

**Fig. 6.** Tropospheric loss rate for hexanal due to UV photolysis and reaction with OH radicals.

were (or were thought to be) very different from that of the *trans* isomer, photoisomerisation cannot be treated as a photodissociation process.

In contrast, for saturated aldehydes the reported quantum yields of photolysis are not negligible, and different photolysis products have been detected (Tadic et al., 2001; Tang and Zhu, 2004). Moortgat (2001) reported a quantum yield of 0.28 for the photolysis of hexanal. For that reason, only the estimation of  $J_1$  values is presented in this section, since  $J_2$  is close to zero.

Photolysis rates of hexanal have been calculated as a function of altitude ( $z$ ) for Ciudad Real, Spain ( $38^{\circ}56'16''\text{N}$ ,  $3^{\circ}55'\text{W}$ ) at noon (June, 2000) by using  $\sigma_{\lambda}$  from Table 1S and assuming for  $\phi_{\lambda}$  the value reported by Moortgat (2001). This situation corresponds to a zenith angle of  $16^{\circ}$ . The actinic

solar flux was calculated by using the Tropospheric Ultraviolet Visible (TUV) model (Madronich and Flocke, 1999). An overhead ozone column and surface albedo were assumed to be 300 DU and 0.1, respectively. We also assumed that the absorption cross section was no temperature dependent.

Estimated  $J_1(z)$  values are listed in Table 4 and plotted in Fig. 6. As it can be seen, the photolysis loss rate ranges from  $1.14 \times 10^{-5} \text{ s}^{-1}$  to  $2.07 \times 10^{-5} \text{ s}^{-1}$ . That means that the tropospheric lifetime due to UV photolysis ( $\tau_{\text{hv}}(1) = 1/J_1$ ) is expected to be less than 2 days. Tang and Zhu (2004) also estimated  $\tau_{\text{hv}}(1)$ , assuming a quantum yield of unity, for a zenith angle between  $0$  and  $60^{\circ}$  to be on the order of 4.5–12.6 h (if  $\phi_{\lambda} = 0.28$  is assumed, 16–45 h). These values are in good agreement with our results obtained at  $\theta = 16^{\circ}$ .

#### 4.2 Estimation of the aldehyde loss rate by OH reaction

The temperature dependences of  $k_{\text{OH}}$  derived from this work were used to estimate the loss rate of hexanal and *trans*-2-hexenal by chemical removal by OH radicals in the troposphere. At a certain temperature  $T$  (corresponding to a certain altitude in the troposphere), this loss rate is defined as the product of the rate coefficient  $k_{\text{OH}}(T)$  and the OH concentration at that altitude. A 24-h averaged OH concentration of  $1 \times 10^6 \text{ molecule cm}^{-3}$  was assumed in these estimations (Krol et al., 1998). In addition, an average environmental lapse rate of  $6.5 \text{ K/km}$  was used to calculate the temperature profile between 0 and 10 km (considering a temperature of 298.15 K at 0 km). In Table 4 the temperature variation as a function of altitude is shown together with aldehyde loss rates. Hexanal loss rate due to the reaction with OH radicals ranges from  $2.79 \times 10^{-5} \text{ s}^{-1}$  at sea level to  $4.74 \times 10^{-5} \text{ s}^{-1}$  near the tropopause. In the case of *trans*-2-hexenal, the loss rate is larger than that of hexanal at all altitudes, as expected taking into account the larger rate coefficients  $k_{\text{OH}}(T)$ .

### 4.3 Tropospheric loss rate for hexanal and *trans*-2-hexenal

The tropospheric lifetime of these aldehydes can be defined as:

$$\tau_i = \frac{1}{J_i + \sum k_{\text{oxid}} [\text{Oxidant}]} \quad (9)$$

In this definition only UV photolysis ( $J_i$ ) and homogeneous reactions with different oxidants (ozone ( $\text{O}_3$ ), nitrate radical ( $\text{NO}_3$ ), OH, and Cl atoms) have been considered.

In general, the reactivity of  $\text{O}_3$  with saturated and unsaturated aldehydes is very slow (less than  $10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) (Atkinson and Arey, 2003; Grosjean et al., 1996). Only the rate coefficient for the reaction of  $\text{O}_3$  with *trans*-2-hexenal has been measured at room temperature by Grosjean et al. (1996) ( $(1.28 \pm 0.28) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). Assuming an average ozone concentration of  $7.4 \times 10^{11} \text{ molecule cm}^{-3}$  (30 ppb) (Logan, 1985), the tropospheric lifetimes at room temperature for hexanal and *trans*-2-hexenal are expected to be more than 10 days. The reaction of hexanal with  $\text{NO}_3$  has been studied at 298 K by D'Anna et al. (2001) by a relative method. The rate coefficient obtained was  $(1.54 \pm 0.19) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . For the corresponding reaction with *trans*-2-hexenal, the reported value for the room temperature rate coefficient by Cabañas et al. (2001) was  $(5.49 \pm 0.95) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Considering an average  $\text{NO}_3$  concentration of  $2.0 \times 10^7 \text{ molecule cm}^{-3}$  (8 ppt) (Finlayson-Pitts and Pitts, 2000), the tropospheric lifetimes of hexanal and *trans*-2-hexenal would be more than one month and 10 days, respectively. Regarding Cl atoms, their reaction with hexanal and *trans*-2-hexenal has been recently studied by Rodríguez et al. (2005) reporting atmospheric lifetimes at 298 K of 8 and 12 days, respectively. As can be extracted from the results in Table 4, the tropospheric lifetimes for these aldehydes due to the reaction with OH at room temperature are about 6 h for *trans*-2-hexenal and 10 h for hexanal. Thus, the chemical removal by other tropospheric oxidants, such as  $\text{O}_3$ ,  $\text{NO}_3$  radicals, and Cl atoms is negligible compared to the reaction with OH radicals. As mentioned above, the photolysis process for *trans*-2-hexenal is negligible, thus, the main degradation pathway for this compound is the reaction with OH radicals. In contrast, the total loss rate of hexanal is defined as the sum of the photolysis rate loss ( $J_1$ ) and the loss rate due to Reaction (R3). These results, together with the estimated tropospheric lifetime ( $\tau_{\text{hexanal}}$  and  $\tau_{\text{trans-2-hexenal}}$ ) as a function of altitude, are shown in Table 4. As can be seen, the tropospheric lifetimes for hexanal and *trans*-2-hexenal are similar at all altitudes. These values ranged from 4 h at 10 km to 7 h at sea level. Even though for both aldehydes the reaction with OH is the major degradation pathway in the troposphere, for hexanal its degradation by photolysis cannot be considered negligible (around 30%).

## 5 Conclusions

In the light of our results, the major tropospheric transformation process for the aliphatic aldehydes, hexanal and *trans*-2-hexenal is the removal by homogeneous reaction with OH radicals. However, the photolysis of hexanal in the actinic region cannot be neglected, since it can account for ca. 30% of the total loss of this compound in the troposphere. In contrast, the fast photoisomerisation described in the literature for *trans*-2-hexenal, instead of a photodissociation process, makes this tropospheric degradation route insignificant.

The observed negative T-dependence of  $k_{\text{OH}}$  for hexanal and *trans*-2-hexenal can be used in modelling the chemistry of the troposphere. The estimated tropospheric lifetimes of these aldehydes decrease with altitude (35% for *trans*-2-hexenal and 42% for hexanal). The assumption of a T-independence of the rate coefficient  $k_{\text{OH}}$  could, therefore, lead to a significant uncertainty in evaluating the impact of these aldehydes in the formation of secondary pollutants.

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